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Particle Phase Distribution of Polycyclic Aromatic Hydrocarbons in Stormwater – Using Humic Acid and Iron Nano-sized Colloids as Test Particles

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Abstract

The distribution of polycyclic aromatic hydrocarbons (PAHs) in different particulate fractions in stormwater: Total, Particulate, Filtrated, Colloidal and Dissolved fractions, were examined and compared to synthetic suspensions of humic acid colloids and iron nano-sized particles. The distribution of low-molecular weight (LMW PAHs), middle-molecular weight (MMW PAHs) and high-molecular weight (HMW PAHs) among the fractions was also evaluated. The results from the synthetic suspensions showed that the highest concentrations of the PAHs were found in the Filtrated fractions and, surprisingly, high loads were found in the Dissolved fractions. The PAHs identified in stormwater in the Particulate fractions and Dissolved fractions follow their hydrophobic properties. In most samples > 50% of the HMW PAHs were found in the Particulate fractions, while the LMW and MMW PAHs were found to a higher extent in the Filtrated fractions. The highest concentrations of PAHs were present in the stormwater with the highest total suspended solids (TSS);the relative amount of the HMW PAHs was highest in the Particulate fractions (particles > 0.7 µm).The highest concentration of PAHs in the Colloidal fraction was found in the sample with occurrence of small nano-sized particles (< 10nm). The results show the importance of developing technologies that both can manage particulate matter but also effectively remove PAHs present in the Colloidal and Dissolved fractions in stormwater.

Keywords: Colloid enhanced transport, liquid – liquid extraction, solid phase extraction, particle sorption, urban stormwater

1 Introduction

During the last decades, growing urbanization and increased anthropogenic activities have turned urban stormwater into a pollution source for receiving waters (Eriksson et al., 2007; Björklund et al., 2011; Barbosa et al., 2012; Deffontis et al. 2013). The concern of pollution of receiving waters has yielded The European Water Framework Directive (2000/60/EC) for protection and restoring of clean water across Europe to ensure its long-term sustainable use. Consequently, pressures exist for implementing efforts in urban areas to collect the stormwater and remove the pollutants closer to the pollution sources, i.e. structural best management practices (BMPs) (Liu et al. 2014). The most frequently applied techniques are construction of artificial wetlands and wet stormwater ponds for sedimentation of particulate pollution (Pitcher et. al. 2004). These treatment facilities are effective if the pollutants are

sorbed to particles which readily settles, i.e. particles > 0.45 µm (Howitt et al., 2014; Bin et al., 2011; Grolimund et al., 2005; Pettersson 1998). However, from recent research, it is clear that pollutants substantially are sorbed onto colloidal particles, and therefore cannot be effectively removed in the treatment facilities operating today (Kalmykova et al. 2013, Nielsen et al. 2015). Several stormwater priority pollutants, notably toxic metals and polycyclic aromatic hydrocarbons (PAHs), have been associated with colloidal material (< 1 µm) in the water (Aryal et al. 2013, Xanthopoulos and Hahn 1990). Kalmykova et al. (2013) have shown that particles < 0.7 µm could considerably contribute to the transport of organic pollutants in landfill leachate, stormwater from urban areas and waste-sorting sites. Despite the documented association of PAHs with colloidal particles, the related particle size distributions (PSD) have not been shown. A greater knowledge of the PSD and general particle characteristics of the colloids transporting the PAHs in stormwater would benefit the targeted development of stormwater treatment facilities, and explain the reasons why PAHs are analysedin receiving waters.

Higher traffic activities have shown a positive correlation with increasing levels of PAHs in stormwater (Moilleron et al., 2002; Murakami et al., 2005; Van Metre et al., 2000). Even though emission control strategies and exchange of fuels have been implemented, increased concentrations of PAHs have been found in urban sediments (Hwang et al., 2006). An important identified source of PAHs in stormwater are highly aromatic (HA) oils added to rubber tires (Wik and Dave, 2005; Norin and Strömvall, 2004).

The categorization of PAHs according to molecular weight follows the definitions by the Agency for Toxic Substances and Disease Registry (ATSDR), under the US Environmental Protection agency (U.S. EPA, 1995): Low-molecular weight PAHs (LMW PAHs) are naphthalene, acenaphthene and acenaphthylene (two and three ring structures), medium-molecular weight PAHs (MMW PAHs) are fluorene, phenanthrene, anthracene, fluoranthene and pyrene (three- and four ring structures). The group of high molecular weight PAHs (HMW PAHs) comprises PAHs with four to six rings, i.e. benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene and indeno[1,2,3-c,d]pyrene. Carcinogenic effects have been quantified for the MMW PAHs and HMW PAHs (Palm et al., 2011). Therefore it is important to study how the PAHs in the different groups are distributed among the Particulate, Colloidal and Dissolved fractions in stormwater. Depending on the different distribution pattern of the groups of

PAHs, combinations of different treatment technologies are needed for sustainable and efficient treatment approaches for the PAHs in stormwater. This may involve a step where larger particles containing most of the HMW PAHs are separated, as for example by sedimentation, combined with techniques for sorbing or oxidizing the dissolved, LMW PAHs, as well as the colloids carrying the MMW PAHs (Kalmykova et al., 2014).

The aim of this study is to investigate the distribution of PAHs associated to nano-sized particles, colloids and particulate matter in urban stormwater, collected at two different stormwater treatment facilities. The collected samples were analysed for the content of LMW PAHs, MMW PAHs and HMW PAHs in the fractions: Total-, Particulate-, Filtrated-, Colloidal- and Dissolved- fractions including nano-sized particles. As the chemical composition of the colloids and the particles, and the particle size distributions in the stormwater samples were unknown, and are expected to vary both in-between and within runoff events, test particles based on documented humic acid nano-sized (HA-n) colloids and nano-sized iron(III) (Fe) particles in suspensions were used as references (Nielsen et al. Submitted), to investigate the distribution of PAHs among the fractions for an organic and inorganic colloid/particle suspension.

The hypotheses were that: i) The PAHs will be distributed in different fractions depending on the molecular weight and, physico-chemical properties of the PAHs, i.e. the HMW PAHs will sorb to particles, the MMW PAHs will be found the colloidal phase and the LMW PAHs in the dissolved phase (Kalmykova et al., 2013), ii) A difference in the groups of PAHs sorbed to the inorganic and organic test particles is expected, due to different sorption pattern(Boyd et al. 2001; Celis et al. 2006; Luo et al. 2008), iii) The amount of PAHs found in the Total fraction will decrease from the inlet to the outlet in the sedimentation pond and the chamber sedimentation facility due to settling, whereas the PAHs in the Filtrated fractions, i.e. Colloidal and Dissolved, it is not expected to differ substantially between the inlet and outlet, since removal of these fractions is not expected in the treatment facilities currently used (Pettersson 1999 Lead et al. 2006).

2 Materials and Methods

2.1 Suspensions and Samples

2.1.1 Preparation of Synthetic Nano-sized Particles

A colloidal suspension with particle sizes of 160 nm in hydrodynamic diameter (HA-n), and a 44 nm in hydrodynamic diameter (Fe) nano-sized particle suspension, derived from iron nitrate, were used as synthetic colloids and nano-sized particles to investigate the sorption of PAHs to an organic and a inorganic entity. Natural organic matter, often consisting of humic and fulvic acids, and quantified as total organic matter (TOC) (e.g. Badin et al., 2008) play an important role in the enhanced transport of pollutants in stormwater, and therefore are HA-n colloids relevant to use as test particles. It is also known that stormwater contains inorganic particles such as natural clay and silt (Grolimund et al. 2005) as well as break-debris particles derived from break wear (Peikertová et al., 2013), and iron has been analysed in high concentrations in road dust (Herngren et al. 2006). Accordingly the use of inorganic Fe nano-sized suspension as test particles is justified. The HA-n colloid and Fe particle suspensions were made following the procedure given by Florence (1982). The mixture of the Fe-n particles and HA-n colloids were found to agglomerate to particles > 200 nm in hydrodynamic diameter. The final HA-n colloid suspension contained 14.4 mg Non-Volatile Organic Carbon (NVOC)/L, with a pH of 7.0 and colloids with an ionic strength of 3.5×10^{-6} mS/cm. The Fe particle suspension contained 47.6 mg Fe/L with a pH of 3.4 and an ionic strength of 0.38×10^{-6} mS/cm. The HA-n colloids and Fe particles are stable over a short time period (<2 months) when stored at +4 °C (Nielsen et al. 2015). For the experiments duplicate suspensions were tested, together with a mixture of the two suspensions (50%/50%), and a Milli-Q water solution (95%/5% V/V Milli-Q H_2O/iso-propanol). The iso-propanol was added to the Milli-Q to better keep the PAHs in the solution, and to avoid PAH sorption to the glass surfaces.

2.1.2 Stormwater Sampling and Sites

Stormwater was collected by multiple grab sampling at Gårda and Järnbrott, two stormwater sedimentation facilities in the area of Gothenburg, Sweden. Samples were collected during two rain events, in the spring of 2013. At the first event only inlet stormwater was sampled (n = 1 for each site), while at the second event both inlet and outlet stormwater were collected (n = 2 for each site), as

multiple grab samples (5 á 2 L) were pooled to yield one composite sample per event, site, and in-/outlet. All sub-samples were stored at < 8 ºC in dark 2 L glass bottles and were extracted within 48 h.

The Gårda stormwater sedimentation facility is situated in Gothenburg city (population ~ 550,000), and is connected to the E6 highway, used by 100,000 vehicles on a daily basis. The catchment is mainly from the trafficked area with ~ 0.051km^2 with 40 % imperious surface. The facility manages stormwater through settling and sedimentation, in seven concrete chambers in series, with a total volume of 122 m^3. The hydraulic retention time is 40 hours, after which the treated water is pumped via a draining pipe to a nearby stream (Pettersson et al., 2005). The inlet samples were collected in chamber 1, and the outlet in chamber 7.

The Järnbrott stormwater facility is a stormwater pond, situated 5 km outside Gothenburg, with a catchment of 30 % commercial/industrial and 70 % residential areas (Pettersson, 1999). The total area is 4.78km^2, with 33 % impervious surface. The area is divided with a city motorway with an annual daily traffic of ~40,000 vehicles. The pond is located in a green area, with a surface area of 6200 m^2, and can contain ~6000 m^3 water, with a maximum inflow of 1100 l/s , the outlet reaches a small stream, which discharges into Kattegat.

2.2 Phase separation

To determine the concentrations of PAHs in the Total, Filtrated and Dissolved fraction (see Figure 1), liquid-liquid extraction (LLE), physical filtration and solid phase extraction (SPE) was used (Kalmykova et al., 2013). Particle- and Colloidal fractions were calculated, using the amounts of PAHs found in the analysed fractions.

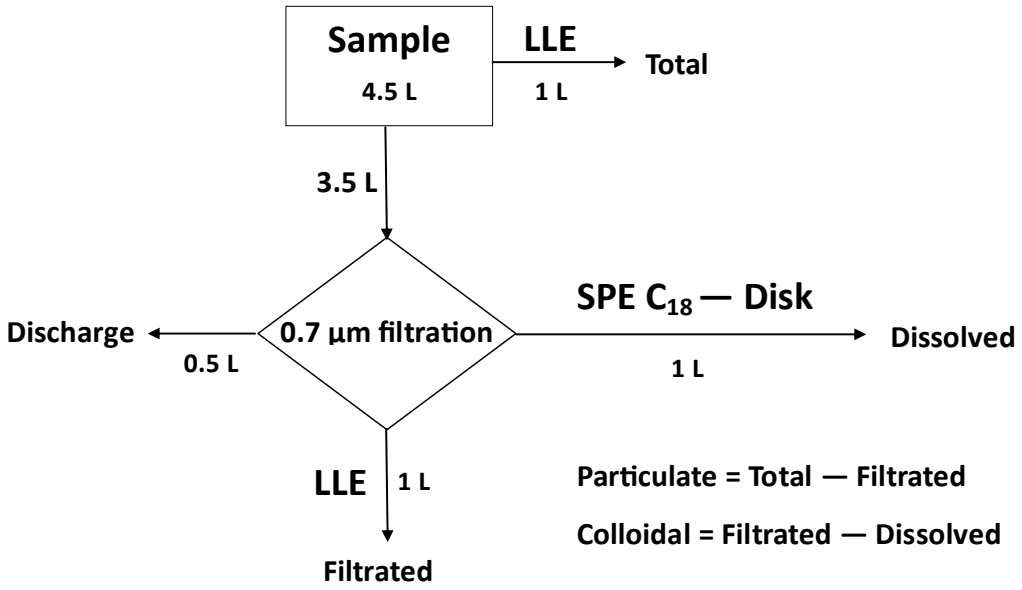

Figure 1: Flow-diagram for separating the nano-sized colloids in suspension, and thereby determine the concentrations of PAHs in the fractions: Total, Filtrated and Dissolved.

A stock solution containing 14 selected PAHs: acenaphthene, acenaphthylene, anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[g,h,i]perylene, benzo[k]fluoranthene, chrysene, fluorene, fluoranthene, naphthalene, phenanthrene and pyrene, was prepared in ethanol with individual concentrations of ~ 210 mg/L. To determine the amount of PAHs in the different fractions, mixtures were prepared by adding 2.5 mL of stock solution to a 4.5 L Milli–Q water or nano-sized and colloidal particle suspension.

2.3 Extraction of PAHs

The mixtures were equilibrated in room temperature for 24 hours, followed by homogenization by shaking before sample aliquots were taken out. The 24 hour equilibrating time was confirmed by Birch et al. (2010), and the biological half-time for the chosen PAHs were in the range of 2 to 2200 days (Wang et al., 2010) assuring that no biological degradation will occur during the experiments. For all experiments an identical filtration and extraction procedure was used following the flow-diagram in Figure 1, and were conducted in duplicates. An aliquot of 1 L was taken for analysis of the concentration of PAHs in the Total fraction by LLE. Here 1 ml of pyrene-d_{10} in acetone (100 mg/L) and 1 ml of perylene-d_{12} in acetone (100 mg/L) were added as internal standards. For the Filtrated and Dissolved fractions, 3.5 L was filtered through a < 0.7 µm binder free glass fibre filter (Whatman®). Of

the filtrated sample (3.5 L), 1 L was taken out for LLE and 1 L aliquots for SPE C_{18}-disc; to each of these, pyrene-d_{10} and perylene-d_{12} were added as internal standards.

The PAHs in the different fractions was determined using the LLE U.S. EPA Method 3510C (1996) and SPE on the C_{18}-disk (Brown et al. 2003). For LLE cyclohexane:ethyl acetate (1:1) was used as solvent, and the extract was cleaned up using a Florisil column to remove polar compounds in the sample (Waksmundzka-Hajnos et al. 1996). The C_{18}-disk (Empore^{TM}) was conditioned, using cyclohexane:ethyl acetate (1:1) and methanol. For the C_{18}-disk a volume of 250 mL could be loaded creating quadrupole loadings in order to yield the nominated 1 L volume. The PAHs was eluted using cyclohexane:ethyl acetate (1:1). All extracts were analysed in duplicates for the 14 specific PAHs, by GC-MS-SIM. The chromatographic separation was conducted on an Agilent 6890 gas chromatograph equipped with a, 60 m x 0.25 mm i.d x 0.25 µm film thickness, ZB-5ms column with a 5 m GuardZ column (Phenomenex). Splitless mode was used, and a 2 µL sample was injected with the injector held at 300 °C. The oven was programmed with a gradient temperature program: start 70 °C, then 20 °C/min to 300 °C, then 50 °C/min to 325 °C held for 10 min. Helium was used as carrier gas with a 1 ml/min constant flow. Detection was achieved on an Agilent 5975C triple-axis mass-selective detector operated in SIM mode with the MS source at 230 °C and the quadrupole at 150 °C.

2.4. Characterization of Stormwater

Dynamic light scattering (Zetasizer Nano ZS, Malvern) measuring in the range from 1 nm to 1000 nm was used to determine the particle size distribution (PSD) in the Filtrated and Colloidal fraction; particles in these fractions were expected to be in the nano-size range. A Coulter Counter, Multisizer^{TM} II, measuring in the range from 2 µm to 50 µm was used to count the number of particles in the Total fraction. Both methods are described in Nielsen et al. (2015). The Zetasizer (Malvern) was also used for measurement of zeta potential (mV) and ionic strength (mS/cm).

Total suspended solids were measured using the same glass fibre filter (0.7 µm) as in the fractionation following the U.S. EPA Method no. 160.2. Element analysis were made on unfiltered samples: aluminium (Al), antimony (Sb), arsenic (As), barium (Ba), cadmium calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), potassium (K), lithium (Li), magnesium (Mg) molybdenum (Mo), manganese (Mn), nickel (Ni), phosphorus (P), lead (Pb), sodium (Na), selenium (Se), silicon (Si), strontium (Sr), sulphur (S), titanium (Ti), vanadium (V) and zinc (Zn), and were

analysedusing ICP-OES: Varian, Vista MPX, after acid digestion according to the Standard DS/EN 13656; NVOC was measured by Shimadzu, TOC-V wp.

2.5. Data analysis and statistical tests

The concentrations of the PAHs were derived from the calibration curve and calculated as averages of duplicates. The µmol loads were corrected according to the internal standard (pyrene-d_{10}). To calculate the percentage distribution (DIS%), the amount in µmol of the PAHs in each of the fractions Particulate, Filtrated, Colloidal and Dissolved (see Figure 1), have been divided with the amount (µmol) of PAHs in the Total fraction. The recovery of the Total fraction was calculated by dividing the spiked amount of PAHs, with the quantified amount of PAHs in the Total fraction. For each fraction the relative percentage (REL%) was calculated for the low-, medium- and high-weighted PAHs based on the total sum of (µmol) PAH. When nothing else is noted, the statistical comparison of measurements was conducted using Students *t*-test, where $p < 0.05$ indicates no statistically significant difference between measurements. The statistical calculations were performed using the Graph Pad Prism Software.

3 Results

3.1 PAHs extractions from synthetic nano-sized colloids and particles in suspension

The distribution of PAHs among the fractions, i.e. DIS% among Total, Particulate, Filtrated, Colloidal and Dissolved, in the three synthetic suspensions containing colloids and nano-sized particles are presented in Table 1, together with the relative composition of the PAHs presented as REL% in Figure 2. In the Milli-Q water spiked with PAHs without added nano-sized particles, 63% of the PAHs in the Total fraction were found in the Particulate fraction. This is explained by sorption of PAHs on the surfaces in the glass-fibre filter. Sorption of PAHs on glass surfaces is a well-known and inevitable problem (Qian et al. 2011); the sorption was shown to decrease with increasing ration of solution volume to contacted surface area (V/S), by using silanized glass and co-solvents. Humic acids were shown to act as co-solvent and increased the solubilisation of volatile organic compounds (Sato et al. 2005). This may explain the lower distribution of 40% PAHs in the Particulate fraction in the suspension containing HA-n colloids. . The loss in the filters were much lower when the colloids were added; therefore it was assumed that the loss due to sorption on the glass-fibre filter will be even lower during filtration of the real stormwater samples, because the glass surfaces are quickly covered by

particles. Losses due to glass surface sorption is not possible to quantify; thus the figures in this study are not corrected for the sorption effect. The low recovery from the Original added (39 µmol) in the Total fractions of 28 – 49%, are also explained by sorption on the glass equipment.

The distribution of the PAHs among the fractions showed that the highest amounts of PAHs were present in the Filtrated fractions in all the synthetic suspensions. This indicates that the PAHs were dissolved or sorbed onto the HA-n colloids and Fe-n particles and, thus, passed through the 0.7 µm filter. Notable, high amounts of the PAHs were found in the Dissolved fraction. For the sample containing Fe particles, as much as 75% of the Total fraction was distributed to the Dissolved fraction. It is possible that the Colloidal phase is underestimated and a part of it measured as Dissolved, as both the HA and Fe particles may be sorbed in the C_{18}-material in the SPE disk.

Table 1. Distribution of PAHs among fractions in the suspensions with different synthetic nano-sized colloids.

		Milli-Q water		Fe-n particles		HA-n colloids		Fe-n particles + HA-n colloids	
	PAHs	**µmol**	**DIS%[a]**	**µmol**	**DIS%[a]**	**µmol**	**DIS%[a]**	**µmol**	**DIS%[a]**
Orginal added	LMW	11		11		11		11	
	MMW	16		16		16		16	
	HMW	23		23		23		23	
	∑PAHs	39		39		39		39	
Total fraction[c]	LMW	3.4		2.2		2.6		3.3	
	MMW	5.9		3.7		5.1		6.1	
	HMW	9.7		5.2		6.1		6.6	
	∑PAHs	19	100(49[d])	11	100 (28[d])	14	100 (36[d])	15	100 (38[d]
Particulate fraction > 0.7 µm[d]	LMW	1.5	44	0.36	16	0.8	31	1.1	33
	MMW	2.6	44	0.66	18	1.9	37	2.8	46
	HMW	7.4	76	2.6	50	2.9	48	3.7	56
	∑PAHs	12	63	3.7	34	5.6	40	7.6	51
Filtrated fraction < 0.7 µm[e]	LMW	1.9	56	1.9	86	1.8	69	2.1	64
	MMW	3.3	56	3.1	84	3.2	63	3.3	54
	HMW	2.3	24	2.6	50	3.2	52	2.9	44
	∑PAHs	7.5	39	7.5	68	8.3	59	8.4	56
Colloidal fraction[f]	LMW	-		0.27	12	0.22	8	0.18	5
	MMW	-		0.27	7	0.43	8	0.46	8
	HMW	-		-	-	-	-	2.1	32
	∑PAHs	-		0.54	5	0-65	5	2.8	19
Dissolved fraction[g]	LMW	2.2	65	1.6	73	1.6	62	1.9	58
	MMW	4.4	75	2.8	76	2.8	55	2.9	48
	HMW	2.6	27	3.9	75	3.3	54	0.79	12
	∑PAHs	9.3	49	8.2	75	7.7	55	5.6	37

[a]DIS%= distribution% calculated from the quantified ∑PAHs (µmol) as well as by LMW PAHs, -M and -H in each Particulate, Filtrated, Colloidal and Dissolved fractions divided with the quantified corresponding mass (µmol) in the Total fraction[c]Total=chemical quantified PAHs in the original sample; [d]The Recovery%= calculated by dividing the ∑PAHs quantified in Total in µmol with the ∑PAHs in µmol added to the original samples; [e]Particulate= calculated as the PAH quantified in Total – PAHs quantified in Filtrated; [f]Filtrated= PAHs quantified in samples after filtration through 0.7 µm glass fibre; [g]Colloidal= calculated as Filtrated PAHs –Dissolved; [i]Dissolved = PAHs quantified on disk SPE.

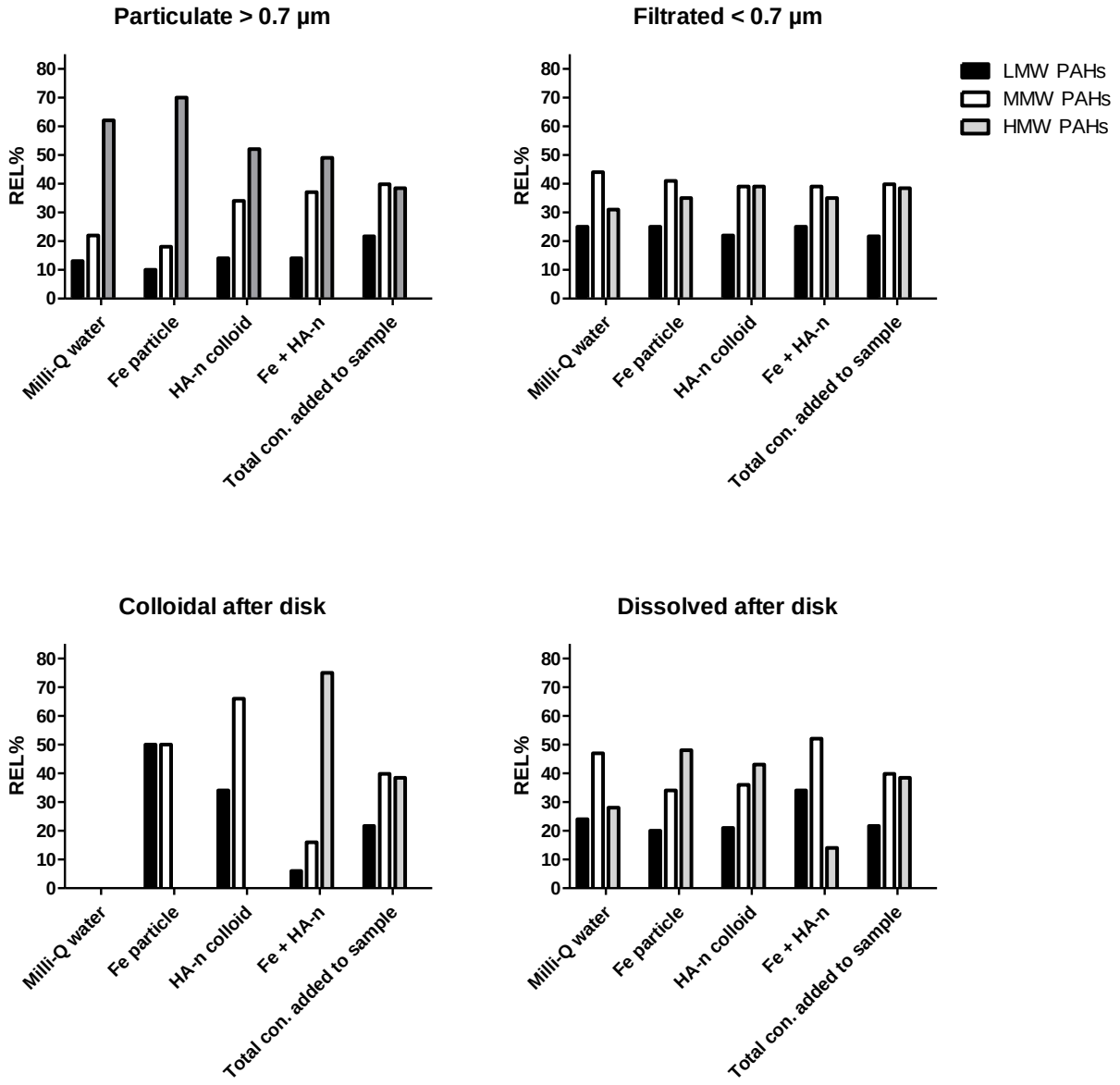

Figure 2: Relative composition (DIS%)[a] of LMW, MMW and HMW PAHs, in the Milli-Q solution and the three suspensions with Fe particles, HA-n colloids and the mixture of Fe particles and HA-n colloids. [a]REL% calculated by the quantified µmol of the LMW PAHs, -M and -H divided with the quantified ∑PAHs in each sample

The relative composition of the LMW, MMW and HMW PAHs were approximately the same in the Filtrated and the Dissolved phases (except for the much lower HMW PAHs for the Dissolved in the Fe+HA suspension). Instead, the HMW PAHs in the Filtrated Fe+HA suspension were found in the Colloidal fraction . The concentrations of PAHs found in the Particulate fractions vs. the Dissolved fractions followed their hydrophobic properties; of the HMW PAHs 50 – 75% was found in the Particulate fractions, while the LMW PAHs and MMH were found to a higher extent, 50 – 75%, in

the Dissolved fractions (see DIS% in Table 1). This is explained by the partitioning and the higher $\log K_{ow}$ of the HMW PAHs and thus a higher ability to sorb to surfaces compared to the LMW PAHs.

3.2 Physico-chemical parameters in stormwater

The stormwater samples were analysed for physical parameters, PSD and concentration of selected metals, see Table 2. The quantifications of TSS from Järnbrott showed lower concentrations compared to Gårda. At Gårda the two inlet samples were quantified to 150 mg/L and 180 mg/L TSS, and an unexpected high TSS at the outlet of 400 mg/L (Pettersson et al. 2005). Even though the TSS increased from the inlet to the outlet, did the PDS, neither the hydrodynamic diameter nor the Coulter counter diameter, show any statistically difference of the sizes of the particles (Table 2). The measurements of pH did not show any statistical difference between samples from inlet and outlet, nor between locations ($p < 0.05$) except for one of the inlet samples from Gårda showing more of an unbuffered rainwater of pH 4.6. The turbidity measured in the inlet sample for Event 2 at Gårda, were found to be significantly different from the rest of the measurements. This could be explained by high turbulence in the underground sedimentation tanks. When the outlet samples were collected, all tanks were filled with water indicating a blockage in the outgoing water. The high water level and heavy rain in the days before sampling could have created turbulence in the tanks, re-suspending some of sediment and thereby given the higher turbidity for the samples.

Table 2: Physico-chemical parameters, particle size distribution and major and minor element concentrations measured in the stormwater.

	Gårda			**Järnbrott**		
	Event 1	**Event 2**		**Event 1**	**Event 2**	
	Inlet	***Inlet***	***Outlet***	***Inlet***	***Inlet***	***Outlet***
pH	6.7	4.6	6.6	7.6	6.9	7.6
EC (µS/cm)	27000	370	290	750	370	440
Ionic strength $\times 10^{-6}$ (mS/cm)	50	5.2	6.4	1.3	7.6	6.8
TSS (mg/L)	150±20	180±3.5	400±7.3	75±1.4	24±6.5	20±0.9
Turbidity (NTU)	90	220	310	90	20	27
Zeta potential (mV)	-18	-22	-21	-24	-22	-26
Hydrodynamic diameter in nm range [a]	39-150	29-95	7.8-170	5.8-230	10-230	16-230
Hydrodynamic diameter in µm range [b]	7.2	4.9	6.5	11	6.2	6.0
NVOC (mg/L)	300	290	270	250	290	270
Concentration of elements (mg/L)						

	Al	1.9	5.4	2.4	1.5	0.47	0.42
	Ca	59	9.1	15	32	23	18
	Fe	5.2	13	5.8	5.3	1.1	1.1
	K	30	5.8	5.3	6.6	46	3.5
	Mg	28	5.4	4.2	6.3	3.5	3.0
	Na	350	36	39	81	42	3.7
Concentration of elements (µg/L)							
	As	BDL	BDL	BDL	BDL	BDL	BDL
	Ba	110	87	54	55	26	21
	Cd	BDL	BDL	BDL	BDL	BDL	BDL
	Co	8.8	13	6.0	2.2	BDL	BDL
	Cr	9.4	25	16	4.8	1.4	BDL
	Cu	110	140	64	53	15	17
	Li	11	9.6	6.0	5.7	3.3	2.9
	Mn	270	220	110	190	58	55
	Mo	13	3.6	2.9	1.9	1.3	BDL
	Ni	9.6	12	6.2	6.1	2.8	2.4
	P	220	350	280	570	84	87
	Pb	5.8	16	7.8	6.3	2.6	2.2
	S	21000	1700	3200	9600	7000	5000
	Sb	7.9	11	6.5	2.7	BDL	BDL
	Se	4.0	BDL	BDL	BDL	BDL	BDL
	Si	8500	11000	8000	6900	6400	6000
	Sn	17	23	15	13	11	8.9
	Sr	280	50	59	100	71	57
	Ti	BDL	BDL	BDL	BDL	BDL	BDL
	V	10	19	8.7	6.7	1.5	1.8
	Zn	350	460	270	220	50	62

BDL = Below Detection Limit (1.3 µg/L), [a] size at 95% accumulated volume (Nielsen et al. 2015)measured with Coulter counter, [b] range given for where nano-particles were observed, when using volume distribution, the samples have been filtrated through a 0.45 µm filter before filtration measured with Zetasizer

The particle size distribution, measured with the Coulter counter showed that the majority of the particles were smaller than 10 µm in diameter, though the accumulated mean diameters were 8 – 12

µm. The Zetasizer measurement showed evidence of nano-particles in all of the samples, but an exact size distribution is not possible to give due to the heterogeneity of the samples (Nielsen et al. submitted). As illustrated in Figure 3, the particle size distributions showed hydrodynamic diameters around 100 nm but the suspensions were highly poly-dispersed hampering accurate interpretations of the distribution curves.

The zeta potential were for all samples found to be negative, though the magnitude of -25 to -17 mV indicates instability (Cho et al. 2012), i.e. prone to coagulate and flocculate. A negative surface charge of the particles, is consistent with particles containing organic acids e.g. fulvic and humic acid and have been documented in literature (Kayhanian et al. 2012, Nielsen et al. 2015).

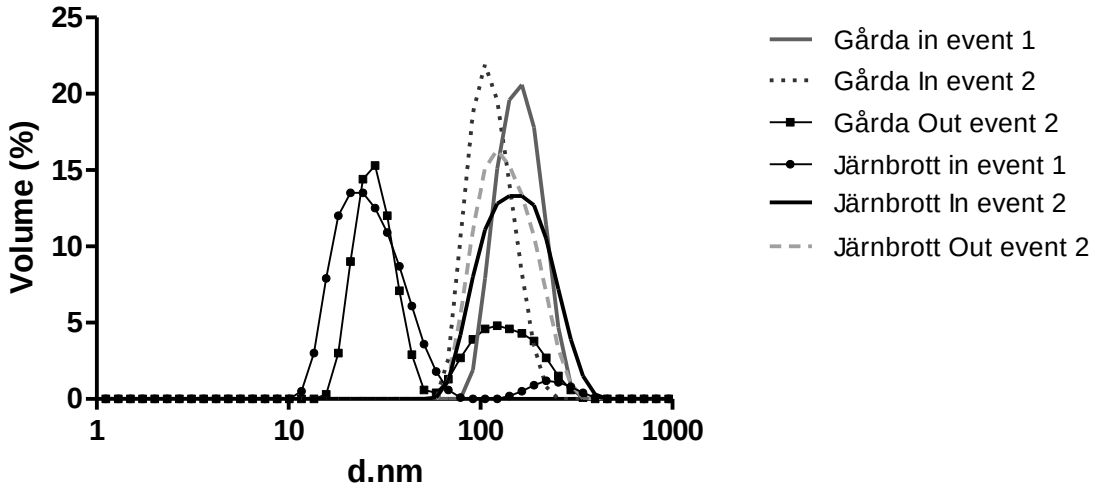

Figure 3: Particle size distribution (PSD) of nano-particles in stormwater measured with a Zetasizer on filtrated samples.

3.4 Polycyclic aromatic hydrocarbons in stormwater

The stormwater samples, presented in Table 3 for Gårda, and Table 4 for Järnbrott, all contained PAHs in concentrations from 3.2 to 139 µg/L. These concentrations were higher than previously reported by Pettersson et al. (2005), where the PAHs-16 at Gårda was ranging in the inlet between 2.6 – 6.9 µg/L, and outlet, between 0.56 – 1.6 µg/L. Comparatively, PAHs measured in urban snow at Gårda was as high as 15 µg/L (Björklund et al., 2011).The high concentrations measured in this study are explained by the relatively long periods of dry weather before sampling, i.e. 8 days before Event 1, and 6 days of dryness before Event 2. During the dry periods, deposition of the pollutants is accumulated on the surfaces and cause high concentrations of pollutants in the stormwater of the coming rain event. Another explanation is that the samples in this study were grab sampled, and the

water sample in the earlier study were taken by flow proportional samplers and yielded event mean concentrations. The PAH concentrations in this study are within the range (<0.01 – 180 µg/L) previously found in stormwater and road runoff, though they notably are in the higher range (Makepeace et al., 1995; Eriksson, 2002; Göbel et al., 2007; Birch et al., 2011). Both parking lot and roof runoff have, however, been quantified with substantially higher PAH concentrations, mainly related to site-specific pollution sources (Eriksson, 2002).

The distribution of PAHs among the fractions in the stormwater (Tables 3 and 4, and Figure 4) showed that high loads of PAHs were found in several of the Particulate fractions at both locations, but the variability was substantial, especially at Event 2 where the Gårda inlet had 32% of the PAHs in the Particulate phase, compared to the outlet where as much as 98% of the PAHs were found on the particles. This is explained by re-suspension of settled sediments caused by the turbulence in the facility during the heavy rain fall, and the thereby much higher value of TSS (Table 2) found in the Gårda outlet samples.

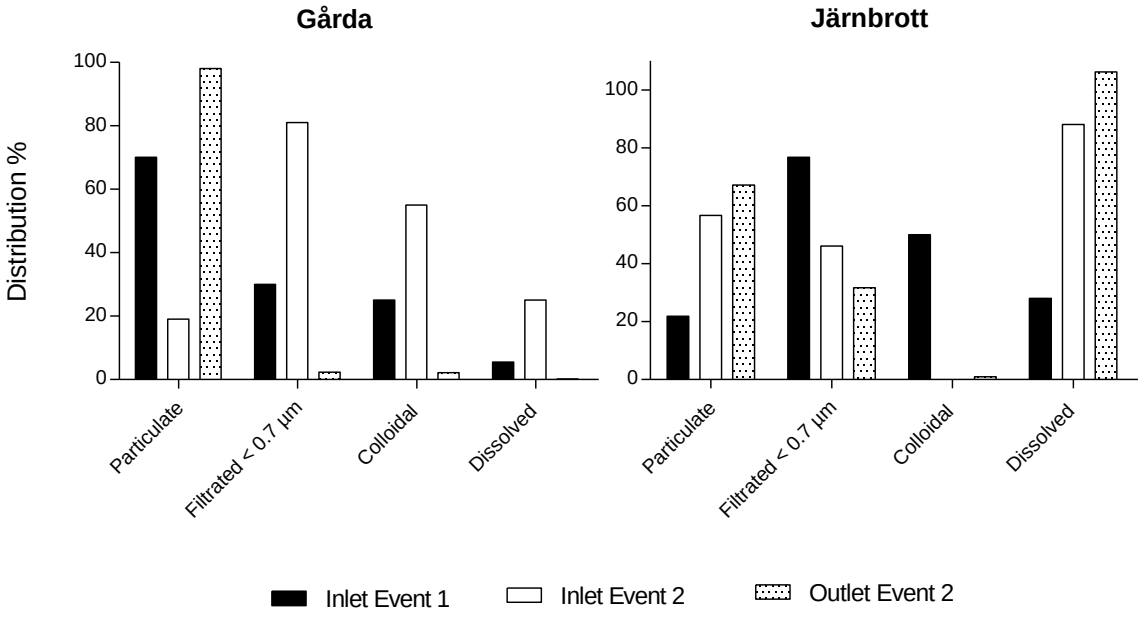

Figure 4: Distribution of PAHs among the different fractions at the two locations.

The PAHs in the Filtrated fractions were lower, but also had a large variability, e.g. from the Event 2 outlet Gårda of only 2.4% PAHs in the Filtrated till the 81% in the inlet sample.. In the Filtrated fractions it was a large difference in the composition of fractions between Gårda and Järnbrott, where samples at Gårda had most of the PAHs in the Colloidal fractions, meanwhile at Järnbrott high concentrations were measured in the Dissolved fraction during event 2. The Gårda samples (event 2, out) had the highest concentration of PAHs in the particulate fraction, and the high

concentrations are explained by the high TSS value in this sample. The Järnbrott sample (event 1, in) with a much lower TSS showed very high amount in the Filtrated and Colloidal fraction; here the occurrence of small particles (< 100 nm) may explain the high concentrations in the colloidal fraction.

The relative composition (Table 3 and 4) show a low proportion of LMW PAHs in the stormwater samples, and especially at the Event 1, which had a long pre-existing dry period (~ 8 days) before the sampling which caused a possible volatilization of the LMW PAHs from the urban surfaces. The samples with the highest loads of the LMW PAHs were the inlet samples at the Event 2 with heavy rain shortly before the sampling; this is as could be expected since the LMW PAHs are the most water soluble and volatile of the 14 PAHs. At both sites the MMW PAHs was dominating, and as earlier reported with a possible sources from both rubber tires and diesel exhausts (Strömvall et al., 2006). The highest amounts of the HMW PAHs were found in the outlet samples for Event 2. Otherwise, the relative loads of the HMW PAHs in the Particulate fractions were highest in the samples with high TSS and the smallest particles (Figure 2), i.e. Gårda out Event 2 and Järnbrott in Event 1. This is explained by the higher $\log K_{ow}$ of the HMW PAHs and their higher ability to sorb to particle surfaces and the high active surfaces of the smallest particles.

Table 3. Distribution of PAHs among fractions, and the relative composition, in samples from the Gårda sedimentation chamber facility.

		µg/L	In Event 1 DIS%[a]	REL%[b]	µg/L	In Event 2 DIS%[a]	REL%[b]	µg/L	Out Event 2 DIS%[a]	REL%[b]
Total fraction[c]	LMW	0.062		0.15	8.9		18	11		8
	MMW	38		94	23		45	64		46
	HMW	2.4		5.8	19		37	63		46
	∑PAHs	40	100		50	100		139	100	
Particulate fraction > 0.7 µm[d]	LMW	0.030		0.11	<d.l.[h]		<d.l.[h]	11		8.3
	MMW	26		92	14		88	61		45
	HMW	2.3		8.1	1.9		12	63		47
	∑PAHs	28	70		9.7	32		135	98	
Filtrated fraction < 0.7 µm[e]	LMW	0.031		0.26	15		37	0.031		0.94
	MMW	12		99	8.9		22	3.2		98
	HMW	0.074		0.61	17		41	0.037		1.1
	∑PAHs	12	30		41	81		3.3	2.4	
Colloidal fraction[f]	LMW	<d.l.[h]		<d.l.[h]	14		50	<d.l.[h]		<d.l.[h]
	MMW	11		100	8.6		31	3.0		100
	HMW	<d.l.[h]		<d.l.[h]	5.4		20	<d.l.[h]		<d.l.[h]
	∑PAHs	10	27		28	56		3.0	2.2	
Dissolved fraction[g]	LMW	0.062		2.8	1.2		9.6	0.031		10
	MMW	0.99		44	0.30		2.4	0.23		77
	HMW	1.2		53	11		88	0.037		12
	∑PAHs	2.2	5.6		13	25		0.30	0.22	

[a]DIS%= distribution% calculated from the quantified ∑PAHs (µmol) in each Particulate, Filtrated, Colloidal and Dissolved fractions divided with the ∑PAHs (µmol) quantified in the Total fraction; [b]REL%= relative% calculated by the µmol of the LMW PAHs, -M and -H divided with the ∑PAHs in each sample; [c]Total = quantified ∑PAHs in the original sample; [d]Particulate= calculated as PAHs quantified in Total – PAHs quantified in Filtrated; [e]Filtrated= PAHs quantified in samples after filtrations through 0.7 µm glass fibre filter; [f]Colloidal= calculated as Filtrated PAHs – Dissolved; [g]Dissolved = PAHs analysed on disk SPE.

Table 4. Distribution of PAHs among fractions, and the relative composition, in samples from the Järnbrott sedimentation pond.

		µg/L	In Event 1 DIS%[a]	REL%[b]	µg/L	In Event 2 DIS%[a]	REL%[b]	µg/L	Out Event 2 DIS%[a]	REL%[b]
Total fraction[c]		0.06	0.08		12	17		0.031	0.96	
	LMW	57	79		19	26		1.9	59	
	MMW	15	21		20	28		1.3	40	
	HMW	71			52			3.2		
	∑PAHs		100			100			100	
Particulate fraction > 0.7 µm[d]	LMW	0.031		0.2	8.3		29	<d.l.[h]		<d.l.[h]
	MMW	3.7		24	19		65	1.4		66
	HMW	12		77	1.6		5.5	0.77		35
	∑PAHs	16	22		28	57		2.2	68	
Filtrated fraction < 0.7 µm[e]	LMW	0.031		0.06	3.9		17	0.062		6.0
	MMW	53		96	0.59		2.5	0.45		44
	HMW	2.3		4.2	19		81	0.51		50
	∑PAHs	55	78		23	46		1.0	32	
Colloidal fraction[f]	LMW	–		<d.l.[h]	3.9		18	0.03		100
	MMW	34		97	<d.l.[h]		<d.l.[h]	<d.l.[h]		<d.l.[h]
	HMW	1.17		3	17		81	<d.l.[h]		<d.l.[h]
	∑PAHs	35	50%		<d.l.[h]	<d.l.[h]		0.3	1.0	
Dissolved fraction[g]	LMW	0.031		0.15	0.031		0.07	0.03		0.9
	MMW	18		94	43		96	1.5		44
	HMW	1.2		5.8	2.0		4.4	1.9		55
	∑PAHs	19	28		45	88		3.5	109	

[a]DIS%= distribution% calculated from the quantified ∑PAHs (µmol) in each Particulate, Filtrated, Colloidal and Dissolved fractions divided with the ∑PAHs (µmol) quantified in the Total fraction; [b]REL%= relative% calculated by the µmol of the LMW PAHs, -M and -H divided with the ∑PAHs in each sample; [c]Total = quantified ∑PAHs in the original sample; [d]Particulate= calculated as PAHs quantified in Total – PAHs quantified in Filtrated; [e]Filtrated= PAHs quantified in samples after filtrations through 0.7 µm glass fibre filter; [f]Colloidal= calculated as Filtrated PAHs –Dissolved; [g]Dissolved = PAHs analysed on disk SPE.

Moreover, the outlet sample of the Event 2 at Gårda contained 139 µg/L PAHs, almost three times the inlet concentration. In contrast, the outlet of the Järnbrott had only about 5% (3.2 µg/L) of the inlet concentration (71 µg/L), see the Discussion section for further details on these findings.

4 Discussion

The results obtained, for both the synthetic suspensions and the stormwater samples, showed that the amount of PAHs found in the Particulate fractions vs. the Dissolved fractions follow their hydrophobic properties. In most samples, > 50% of the HMW PAHs were found in the Particulate fractions, while the LMW and MMW PAHs were found to a higher extent in the Filtrated fractions. In the synthetic suspensions, presence of colloids caused even the most hydrophobic HMW PAHs to be found more equally represented in the Filtrated and the Particulate fractions, which supports the finding by Kalmykova et al. (2013) that PAHs partition to the Particulate fraction is reduced in the presence of colloids. This effect is in accordance with the molecular weight and hydrophobicity of the compounds i.e. the partition to the Filtrated = Colloidal + Dissolved fraction show a negative correlation with $\log K_{ow}$. Hypothesis (i) is strengthen by the results from the stormwater, as the samples from Event 2 with heavy rain fall before sampling, contained more of the water soluble LMW PAHs; the relative amount of the HMW PAHs were also highest in the samples with high TSS, which also contained small particles.

For hypothesis ii) the amount of PAHs sorbed on inorganic particles (Fe) was about 50% of the loads sorbed on the organic particles, the Fe + HA and HA suspensions, respectively (Table 1, Particulate fraction). The difference was almost entirely due to the much lower LMW and MMW PAHs sorption to Fe particles. This suggests that the most hydrophobic HMW PAHs partition to Fe particles, while the LMW and MMW PAHs remain in the Dissolved fraction, which potentially enhances their mobility. Among the Colloidal suspensions, the Fe + HA combination have resulted in the highest particulate-bound PAHs, probably due to formation of the larger particles due to Fe and HA agglomeration, as was shown in Kalmykova et.al. (2010) and Nielsen et al. submitted. The Fe-n particles had a size of 44 nm in hydrodynamic, while the HA-n colloids were found to be 160 nm in hydrodynamic diameter. The Fe + HA combination have also resulted in the highest Colloidal fraction, which is even more mobile than the Dissolved fraction.

For the third hypothesis iii) the amount of PAHs found in the Total fraction should be decreasing from the inlet to the outlet in the settling facilities. For the Gårda facility this hypothesis can be rejected, but not for the Järnbrott pond. In fact, the highest concentration of PAHs at Gårda was

found in the outlet of the Event 2, and it was threefold higher than the inlet concentration for the same event. Extreme situations like event 2 at Gårda (heavy rain, and sediment re-suspension) are unthinkable to use for evaluation of the treatment efficiencies, which require data for extended seasons, different types of events as described by intensity and duration, and sampling schemes adjusted according to the systems hydraulic retention time. Here, however, the results from Gårda highlight that during extreme situations more particulate matter than anticipated can be discharged, and with it, toxic trace metals, Table 2, and PAHs in the Particulate fraction, Table 3. At Järnbrott, a tenfold decrease of the outlet concentration of PAHs compared to the inlet concentration was observed (Table 4). The biggest decrease is seen for the Filtrated fraction, where the concentration has decreased 23-fold. Low concentrations of Colloidal-bound PAHs were found in the Järnbrott outlet that indicates that the pond, during the prevailing weather conditions, was working effective. However, repeated analysis is needed to confirm the ponds efficiency due to the large variability of the inlet composition, i.e. 77% of PAH were found in the Colloidal fraction in the inlet of the Event 1, which may lead to a different removal efficiency compared to the Event 2.

Relatively high amounts of HMW PAHs were found in the Järnbrott outlet.. Non-volatile organic carbon, representing the organic matter in the stormwater was analysed in all the samples and showed no statically significant difference between inlet and outlet samples. Therefore the higher amount of HMW PAHs in the outlet at Järnbrott can not be explained by the sorption to elevated concentration of dissolved organic matter. An increase in the NVOC concentration in the outlet compared to the inlet, due to enrichment in the pond, could otherwise have affected the result, as the presence of DOC is proven to decrease the partition of PAHs to larger particles (Kalmykova et al. 2013).

5 Conclusions

The stormwater in this study is polluted with PAHs originating from the highway runoff with concentrations in the higher range of the previously internationally reported levels. Substantial part of this pollution has been found in the Filtrated fraction, which may be difficult to retain by the conventional stormwater techniques, presented here by the sedimentation pond (Järnbrott) and a chain of sedimentation chambers (Gårda). In the Järnbrott pond, a tenfold decrease of the outlet concentration of PAHs compared to the inlet were found. Yet, a non-negligible PAHs concentration in the outlet sample, mainly found in the Dissolved fraction, may pose a risk to the environment. On

the other hand, in the sedimentation chambers, the outlet concentration was higher than the inlet, due to the re-suspension of the PAHs bound to sediment during the turbulent conditions of the heavy rain. This highlights the risks of secondary pollution from the sedimentation-based systems.

The study of the PAHs distribution in the synthetic suspensions has confirmed considerable distribution of the PAHs to Filtrated fractions and clarified the role of the studied particle suspensions in the PAH distribution. It has been shown that the PAHs are distributed among the fractions differently depending on the molecular weight; the LMW and MMW PAHs were mostly found in the Filtrated fractions, while more of the HMW PAHs has been found in the Particulate fractions. The Filtrated fraction was mostly constituted of the Dissolved pollutants, except for the Fe+HA suspension, where Colloidal fraction was significant. The fact of such significant presence of PAHs in Filtrated fraction potentially enhances their mobility. The amount of PAHs sorbed to the mixture of the Fe-HA particles was the highest, while to the inorganic Fe particles – the lowest.

The results with high amounts of PAHs in the Filtrated fractions, observed for both the synthetic solutions and the stormwater, show the importance of development of advanced techniques for stormwater treatment that are able to remove the PAHs in the colloidal and dissolved phases. In particular, the stormwater treatment technologies needs to be complemented with techniques that are able to reduce the dissolved PAHs, e.g. sorption filters, and colloidal-bound PAHs by for example oxidation, ozonolysis or UV-degradation.

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